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ENVIRONMENTAL CONTAMINANTS DIVISION

NATIONAL WATER RESEARCH INSTITUTE

CURRENT RESEARCH

MARCH 1984

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FOREWORD

Research accomplishments of the staff of the Environmental Contaminants Division, National Water Research Institute, are reported annually in Current Research. Each study is described separately by the study team. The reports complete an annual cycle which is initiated with the publication of Study Plans, twelve months prior to this report. These Study Plans say what we expect to do and why during the upcoming fiscal year. During the year, six- and nine-month reports on each study are prepared internally for management control of resources. These reports are brief and include shifts in direction or problems encountered. Finally CurrentResearch is prepared in the last month of each fiscal year and describes accomplishments only. Current Research says what we have done and includes references to all reports or publications prepared under each study since the last issue of the previous March.

R.J. Allan
Editor

CITING PROCEDURE

Articles in this report should be cited as follows:

"Oliver, B.G. and Nicol, K.D. 1984. Chlorinated Hydrocarbons in Water, Sediments and Biota of the Great Lakes. in Current Research, Environmental Contaminants Division, NWRI, p. 37-39."

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ENVIRONMENTAL CONTAMINANTS DIVISION

RESEARCH PROGRAM

by

R.J. Allan

Contamination deleteriously affects many uses of Canada's freshwater resources. Action to alleviate public concern about contamination and/or to reduce or eliminate contamination is predicated by in-depth knowledge of the fate of contaminants in aquatic ecosystems. The Environmental Contaminants Division (Tables 1 and 2) investigates five groupings of contaminants - organic chemicals, usually of industrial or agricultural origin; toxic metals; organometallics; ions associated with acid rain; and radionuclides. Division activities are carried out in five sections (Table 1) as follows:

Organics-Pathways Section

The objective is to resolve the entry, fate, distribution, and transfer of organic contaminants in aquatic ecosystems. Research is conducted primarily at specific polluted aquatic ecosystems but also in the laboratory. Projects include studies in large and small river-lake systems. Atmospheric input of organic contaminants to the aquatic environment is also being studied.

Organics-Properties Section

The objective is to investigate, primarily in the laboratory, the physical-chemical characteristics of organic chemicals which govern their interactions with biota and abiotic material in aquatic ecosystems. Structure-activity (property - biological effect) correlations are established for a variety of contaminants with a view to establishing general underlying

TABLE 1. ENVIRONMENTAL CONTAMINANTS DIVISION ORGANIZATION

Chief - Dr. R.J. Allan
Secretary - Mrs. E.M. Kerr
Administrative Officer - Mr. F. Boyd

. Applied geochemistry

ORGANICS-PATHWAYS SECTION

Head - Dr. J.H. Carey • Photodegradation of organic contaminants.

Researchers:

Mr. M.E. Fox • Persistent organic contaminants in aquatic ecosystems.

Mrs. J.L. Metcalfe • Biological fate of contaminants.

Dr. E. Nagy • Fate and effects of herbicides.

Dr. W.M.J. Strachan . Organic contaminants in aquatic ecosystems, especially rain.

Technologists:

Miss L. Coletta, Mr. J.H. Hart

ORGANIC-PROPERTIES SECTION

Head - Dr.K.L.E. Kaiser . Structure-Activity correlations of organic contaminants.

Researchers:

Dr. R.M. Baxter . Biochemistry and degradation products of PCBs.

Mrs. K. Kwasniewska . Biodegradation of organic contaminants and toxicity to microorganisms.

Dr. D.L.S. Liu . Biodegradation of organic contaminants.

Dr. B.G. Oliver • Sources of aquatic organic organic contaminants, water chlorination. by products.

Post Doctoral Fellow:

Dr. J.M. Ribo • Structure-activity correlations of organic

Technologists:

Mr. M.E. Combe, Mrs. K.D. Nicol, Mrs. K. Thomson.

INORGANICS SECTION

Head - Dr. R.J. Maguire • Aquatic fate of organometallics.

Researchers:

Dr. Y.K. Chau • Chemical and biological processes of organometallics in the aquatic environment, metal speciation and toxicity.

Dr. K.R. Lum • Chemical forms of trace metals and geochemistry of particulate matter.

Mrs. A. Mudroch . Biomassays and geochemistry of sediments.

Technologists:

Mr. G.A. Bengert, Mr. R.J. Thacz., Miss E. Kokotich.

ACID DEPOSITION SECTION

Head - Dr.D.S. Jeffries . Geochemical processes controlling lake acidification; metal geochemistry.

Researcher:

Mr. R.G. Semkin . Geochemical processes controlling lake acidification.

Post Doctoral Fellow:

Dr. M. English . Snow chemistry.

Technologists:

Miss M.D. Jones, Mr. J. Longlade, Mr. R. Maureuther.

RADIONUCLIDES SECTION

Head - Dr. S.R. Joshi • Aquatic pathways of radionuclides.

Researcher:

Dr. R.F. Platford • Physical chemistry of radionuclides.

Technologists:

Mr. J.A. FitzGerald, Mrs. S.P. Thompson.

December 1983

Table 2. Environmental Contaminants Division Professional Staff

Dr. R.J. Allan
B.Sc. (Aberdeen); M.S. (Wisconsin); Ph.D. (Dartmouth): D.Sc. (Aberdeen).

Dr. R.M. Baxter
B.Sc. (Mt. Allison); Ph.D. (McGill).

Dr. J.H. Carey
B.Sc. (Windsor); M.Sc. (Windsor); Ph.D. (Carleton).

Dr. Y.K. Chau
B.Sc. (Lingnan); M.Sc. (Hong Kong); Ph.D. (Liverpool); D.Sc. (Liverpool).

Mr. M.E. Fox
B.Sc. (Mt. Allison).

Dr. D.S. Jeffries
B.Sc. (McMaster); Ph.D. (McMaster).

Dr. S.R. Joshi
B.Sc. (Punjab); M.Sc. (Roorkee); Ph.D. (Roorkee).

Dr. K.L.E. Kaiser
B.Sc. (Munich); M.Sc. (Munich); Ph.D. (Munich).

Mrs. K. Kwasniewska
M.Sc. (Marie Curie).

Dr. D.L. Liu
B.Sc. (Chung-Hsing); M.Sc. (U.B.C.); Ph.D. (U.B.C.).

Dr. K.R. Lum
B.Sc. (Manitoba); Ph.D. (Liverpool).

Mrs. J. Metcalfe
B.Sc. (Manitoba).

Dr. R.J. Maguire
B.Sc. (Ottawa); Ph.D. (Alberta).

Mrs. A. Mudroch
Dipl. Chem. (Prague); M.Sc. (McMaster).

Dr. E. Nagy
Dipl. Chem. (Debrecen); M.Sc. (Saskatchewan); Ph.D. (Saskatchewan).

Dr. B.G. Oliver
B.Sc. (Manitoba); M.Sc. (Manitoba); Ph.D. (Manitoba).

Dr. R.F. Platford
B.A. (U.B.C.); M.Sc. (U.B.C.); Ph.D. (Saskatchewan).

Mr. R.G. Semkin
B.Sc. (Toronto); M.Sc. (McMaster).

Dr. W.M.J. Strachan
B.A. (Toronto); M.A. (Toronto); Ph.D. (Queens).

principles of chemical properties and effects. Bulk properties such as lipid-water or sediment-water partition coefficients and processes or reactions such as hydrolysis, photodegradation and bioaccumulation are measured. The toxicity of organic chemicals to bacteria and fungi is examined. The biodegradation of organic chemicals is determined in controlled laboratory environments.

Inorganics Section

The objective is to determine the fate of inorganic contaminants in aquatic ecosystems. Laboratory studies on properties and transformation of various organometallics, such as organolead and organotin compounds are correlated with field measurements at polluted sites in Canada. The distribution, pathways, bioavailability and processes controlling these for toxic metals in large river-lake systems are investigated.

Radionuclides Section

The objective is to study the behaviour of aquatic ecosystems of both naturally occurring and artificial radionuclides. Studies include the determination of pathways of radionuclides discharged to rivers and lakes during nuclear fuel cycle operations; determination of concentrations of these radionuclides in water, selected biota, and sediments to assess the radiological dose to organisms; the verification of predictive models for the dispersion of radionuclides into ground and surface water; and the measurement of concentration profiles of certain radionuclides in lake sediments to provide a time-scale for determining the lifetimes of other contaminants in aquatic ecosystems.

Acid Deposition Section

The geochemical controls of lake acidification and the response of drainage basins to airborne deposition of ions associated with acid precipitation is studied in a calibrated watershed. Emphasis is on the spring snow melt event and on the chemistry of snow packs. The influences of acid precipitation on metal availability are examined.

Although the objectives of each Section are separated above, there is often overlap between projects in different Sections. Information arrived at in one Section can be valuable to the achievement of goals in another Section. No individual project can lead to a complete understanding of the fate and impact of a contaminant released to an aquatic ecosystem. Information from several projects can also lead to predictive modelling of the fate of new contaminants.

APPROACH TO THE ISSUES

Toxic Chemicals

Toxic contaminant research is often referred to as toxic substance characteristics in the terminology of international and national agencies dealing with toxic chemicals control. The Division program determines such characteristics. The meaning of the term characteristics can best be described by dividing it into two sub-categories. These are: (1) field characteristics of chemicals in actual polluted aquatic ecosystems (i.e., data describing the real fate and actual factors and processes controlling this fate in such ecosystems), and (2) laboratory characteristics such as physical-chemical properties, laboratory tests of aquatic toxicity, bioaccumulation, biodegradation and related parameters (i.e., data which may help to allow prediction of aquatic ecosystem fate of toxic chemicals). Environmental Sensing, a new term now being used, includes such research.

The emphasis of the aquatic science, toxic chemical research in ECD is (1) above because most of the issues NWRI has to respond to concern how to manage already polluted river-lake ecosystems or systems with a potential for pollution. The prime examples are Canada's Great Lakes. Others are the Wabigoon River System, Ontario; the Fraser River, B.C.; the North Saskatchewan; the Shubenacadie Headwaters Lakes, Nova Scotia etc. Specific answers to chemical specific questions at these sites could never be adequately resolved by laboratory testing alone. The types of scientific questions resolved concern the effect on chemical fate of particulate-water interactions; biota-water-particulate interactions; air-water interactions; and degradation processes and products. Identification of chemicals is an additional aspect of the field programs. Laboratory tests are conducted to complement or enhance conclusions arrived at by the extensive field programs necessary for resolution of specific recommendations as to control of effluents or changes in basin water management practices.

The Division is also involved in the determination of laboratory characteristics as mentioned under (2) above to: (a) help resolve conclusions arrived at from field operations as to processes controlling fate of and thus exposure to chemicals; (b) help develop and standardize new techniques for laboratory testing of physical-chemical properties; (c) to provide physical-chemical and various biodegradation, bioaccumulation, aquatic toxicity parameters on high priority chemicals, where the measurements are unique and not of a routine nature.

For any specific chemical, the research results on toxic chemical characteristics in actual polluted ecosystems and the laboratory determined "properties" or "characteristics" are interpreted and published in the scientific literature where they are used to make specific recommendations on specific issues and as input to the chemical Assessment process.

ECD initiates its specific or chemical specific research on the basis of internal and external stimuli. Internally the scientific decisions are often supported by an external agency or public interest. The field sites which receive intensive investigation usually become obvious because of public concern about pollution issues. Chemical priorities usually also become rapidly evident because of the concerns about water pollution by specific chemicals. Examples are dioxins because of the waste dumps near the Niagara River; chlorinated benzenes, for the same reason; PCB's and toxaphene because of their levels in Lake Superior fish; mercury because of its presence in the Wabigoon River and so on. There are thus major overlaps between basin management issues viz toxic chemicals and priority chemicals per se.

The research information produced by the Division can in itself be valuable in substantiating recommendations for water management actions in polluted river basins. These actions may involve control of effluents, banning of chemicals, guidelines for consumption of biota or water, and many other procedures which can be implemented in Canada. Data may be valuable in negotiations on water quality matters either interprovincially or internationally. Much of the published information is equally valuable as part of the total input required for toxic chemical assessments. Various actions on the control of chemicals are usually the result of extensive, iterative, assessment procedures. ECD does not by any means supply all the information required. Input from many other disciplines and agencies is required, particularly those dealing with aquatic and mammalian toxicology.

Acid Rain

The Division program aims at understanding the geochemical controls or buffers to acid precipitation in stream-lake systems. For this purpose, mass balance models are based on sampling of a calibrated watershed located near Saulte Ste. Marie. The basin research is managed by a Steering Committee presently chaired by Dr. D. Jeffries of ECD. The basin contains seven lakes interconnected by streams. The work is in association with programs of other agencies including CFS, DFO, NHRI, and

Lands Directorate. The data derived from this multi-agency, multi-disciplinary research is complementary.

Most studies of acid rain deal with the effects of acid rain. The Division aim is not to measure effects but to resolve: (a) long-term rates of acidification, and (b) buffering processes. The goal is to define how fast a river-lake system becomes acidified and what characteristics control this rate. The results are expected to lead to a better calculation of how rivers and lakes can withstand, for how long, the ionic species associated with acid rain and what parameters control this. Airborne emission control requirements may then be more accurately defined.

COMMITTEE AND EDITORIAL BOARD INVOLVEMENT

ECD staff are involved in a variety of regional, national and international committees (Table 3). ECD staff are also represented on the Editorial Boards of scientific journals (Table 4).

Acronyms in Table 3.

GLWQA = Great Lakes Water Quality Agreement;
OECD = Organization for Economic Cooperation and Development;
ECA = Environmental Contaminants Act;
DOE = Department of the Environment;
NHW = National Health and Welfare Department;
NRC = National Research Council;
IJC = International Joint Commission (U.S.-Canada);
SAB = Science Advisory Board;
NSERC = National Sciences Engineering and Research Council;
ASTM = Analytical Standards for Testing of Materials;
UN-FAO = United Nations - Food and Agriculture Organization;
WQB = Water Quality Board;
AGRAD = Agricultural Research and Development Committee;
TFM = 3-Trifluoro-4-nitrophenol;
ESTER = Testing and Hazard Evaluation of Chemicals in Aquatic Environments.

TABLE 3. ECD COMMITTEE INVOLVEMENT

Allan, R.J.(Co-Chm)	Canada Ontario Wabigoon River Mercury Pollution (CWA)
Allan, R.J./Strachan, W.M.J.	GLWQA Toxic Contaminant
Carey, J.H.	NRC Environmental Secretariat Panel on TFM
Chau, Y.K.	NSERC Strategic Grant Selection Panel on Environmental Toxicology
Chau, Y.K./Liu, D.	Standards Council of Canada
Chau, Y.K./Mudroch, A.	IJC/SAB Task Force on Ecological Effects of Sediment Contaminants
Jeffries, D.S.(Chm)./Allan, R.J.	Turkey Lakes Watershed Acid Rain Steering
Joshi, S.R.	DOE Nuclear Advisory
Kaiser, K.L.E.	IJC - SAB Task Force on Non-Phosphate Detergents
Liu, D.L.S.	ASTM Oxygen Uptake Group
Liu, D.L.S.	UN-FAO Marine Fouling Group
Maguire, R.J.	Environmental Monitoring of Forest Insect Control
Maguire, R.J./Chau, Y.K.	NRC Environmental Secretariat Panel on Oganotins
Maguire, R.J./Strachan, W.M.J.	ECA Chemical Evaluation
Maguire, R.J.	Interdepartmental Working Group on ECA Amendments
Mudroch, A.	Canada/U.S. Niagara River Study
Mudroch, A.	DOE Schubenacadie Lakes Study Group
Oliver, B.G.	DOE Review Group on Drinking Water Safety
Oliver, B.G.	Data Quality, Niagara River Toxics Committee
Strachan, W.M.J.	OECD Chemical Testing Program
Strachan, W.M.J.(Chm)	GLWQA Aquatic Ecosystem Objectives
Strachan, W.M.J.	DOE/NHW Environmental Contaminants
Strachan, W.M.J.	Swedens ESTHER Program Evaluation
Strachan, W.M.J.	IJC/SAB Task Force on Modelling
Strachan, W.M.J.	IJC/WQB Assessment Coordination

TABLE 4. ECD EDITORIAL BOARD INVOLVEMENT

Allan, R.J.	• Water Pollution Research Journal of Canada, Editor-in-Chief • World Health Organization, Water Quality Bulletin, Editorial Board
Chau, Y.K.	• Journal of Great Lakes Research, Associate Editor • Water Pollution Research Journal of Canada, Editorial Board
Jeffries, D.S.	• Water Pollution Research Journal of Canada, Editorial Board
Kaiser, K.L.E.	• Journal of Great Lakes Research, Associate Editor
Liu, D.	• Toxicity Assessment Bulletin, Co-Editor
Oliver, B.G.	• Environmental Toxicology and Chemistry, Editorial Board • World Health Organization Water Quality Bulletin, Editorial Board • Water Pollution Research Journal of Canada, Editorial Board

FUTURE DIRECTIONS

The present ongoing activities of the Division and the philosophy behind them have been briefly described above. Shifts for 1984/85 and the immediate future are described below.

The Division program is an integral part of work conducted under the Great Lakes Water Quality Agreement. The major site of interest has been the Niagara River and Lake Ontario. Work in this area will be reduced. Research was initiated in 1983/84 on the contaminant problems in the Detroit River/Lake St. Clair/Lake Erie system and will continue in 1984/85. A study group, led by Dr. Y.K. Chau was established to coordinate ECD projects. Research on atmospheric deposition of toxic organic chemicals will continue with the focus on toxaphene in Lake Superior but monitoring sites will be added in Alberta and New Brunswick.

The research on the fate of chlorophenols and other chemicals in Canagagigue Creek, Grand River Basin, will end. The conclusions arrived at will be the basis for contaminant fate research in the Fraser River, B.C.; the North Saskatchewan River in Alberta; and the Qu'Appelle River in Saskatchewan. The toxic metals fate research on the Great Lakes, will be expanded to involve the arsenic/acid mine drainage issue problem in the Schubenacadie Headwaters Lake system of Nova Scotia. The radionuclides pathways research program, also focused on the Great Lakes and in Ontario, will again include research near major uranium deposits and mining operations in northern Saskatchewan.

In terms of laboratory characteristics, emphasis on Structure-Activity Relationships will continue to shift from toxicology using fish to the development of simpler, more rapid toxicity tests using lower organisms such as yeasts and bacteria. Determination of specific physical-chemical properties of chemicals for assessment purposes will focus, if feasible, on those chemicals with which there are existing concerns, e.g., chlorinated di-benzo dioxins and furans; PCBs; chlorinated benzenes and phenols; toxaphene; organotins; alkyl leads; methyl-Hg; Cd; As; and Pb.

The acid rain program will de-emphasize the intensive sampling program because three years of data are now on file. The shift towards investigation of processes such as aging of snow packs and aluminum shock will continue.

The Division will continue to actively seek external funding to support our program. There were four such sources of support in 1983/84: the Great Lakes Water Quality Toxic Contaminant Program (GLWQA); the Long-Range Transport of Atmospheric Pollutants Program (LRTAP); the Toxic Chemicals Management Program (TCMP); and the Baseline Studies Program.

The remainder of this issue of Current Research consists of brief descriptions of the scientific advances made in each ECD project. Some figures and tables are included to give an idea of the type of information contained in the many papers and reports published by the Division and in the documents produced by committees on which Division staff serve.

A. **PRIMARILY PROJECTS RELATED TO TOXIC CONTAMINANTS IN THE DETROIT RIVER AND NIAGARA RIVER SYSTEMS AND FATE IN POLLUTED AQUATIC ECOSYSTEMS OF VOLATILE ORGANICS, TOXIC METALS, ORGANOMETALLICS, CHLORINATED ORGANICS AND RADIONUCLIDES.**

CONTAMINATION OF LAKE ONTARIO BY PERSISTENT ORGANICS FROM THE NIAGARA RIVER

by

M.E. Fox, J.H. Carey and P.A. Coletta

INTRODUCTION

1982/83 saw the completion of the part of the study involving incorporation of organochlorine contaminants from the Niagara River into Lake Ontario sediments, fish and biota. This resulted in a publication (1) discussing the compartmental distribution of ten chlorobenzenes, hexachlorobutadiene and PCB's. Strong correlations were observed between sediment/water concentration ratios and published octanol water partition coefficients for the compounds studied. A relative accumulation factor concept was developed which allows an approximate prediction of the relative accumulation of specific contaminants in the different compartments.

The second part of the study is an investigation of the kinetics of dispersion of selected contaminants between the dissolved and particulate phases in the Niagara River plume. The 1982/83 data showed that dissolved contaminants such as 1,2,3,4-tetrachlorobenzene were almost entirely transported out of the river mouth area in solution (90%). A more detailed sampling grid and larger samples were required to refine the analytical data and permit calculation of the dynamics of distribution.

RESEARCH RESULTS

A new sampling grid consisting of 36 stations in a rectangular pattern 10 x 14 km was designed in collaboration with staff of APSD. Samples were collected on this grid on three occasions in 1983: May 11, August 10 and October 4. Niagara River mouth samples were collected at the beginning and end of the sampling period (about 12 hr) and the staff of APSD deployed

drogues to map the plume dispersion concurrently with the water sampling.

Two water samples of 4 L each were collected at 1 and 5 m at each site with one sample being filtered in situ. Optical transmission and temperature were measured at each site and the filters retained for further investigation.

The May and October sampling cruises found the plume to be following its most common track which consists of an easterly flow along the south shore of Lake Ontario, less than 10 km offshore. In both of these events the water sampling and drogue movement managed to remain concurrent over much of the 12 hr sampling period. This facilitated the following of a discrete water mass and avoided problems related to variations in contaminant levels in the river inflow.

In August the sampling event coincided with a less common plume track flow westerly for a few km and then flowing straight offshore in a northerly direction. Rough weather made sample collection and drogue track matching difficult.

Work is proceeding on data interpretation and early results tend to confirm 1982/83 findings that organochlorine contaminants are largely transported out of the river mouth area in solution and hence may travel considerable distances in the lake.

In 1984/85, the sampling programme will end with an attempt to follow the dispersion of selected organochlorine contaminants still further with the aid of 'talking' drogues which may be tracked by shipborne radio or satellites. Larger samples will be required to offset the dilution processes and different analytical techniques are currently under investigation.

PUBLICATIONS

1. Fox, M.E., Carey, J.H. and Oliver, B.G. Compartmental distribution of organochlorine contaminants in the Niagara River and the Western Basin of Lake Ontario. J. Great Lakes Res. 9(2):287-294.

2. Fox, M.E. and Joshi, S.R. The fate of pentachlorophenol in the Bay of Quinte, Lake Ontario. J. Great Lakes Res. 10(2):190-196.

3. Joshi, S.R. and Fox, M.E. The ^{210}Pb and ^{137}Cs profiles in sediment cores from the Bay of Quinte, Lake Ontario. Accepted by J. Radio Anal. Chem.

4. Carey, J.H., Fox, M.E., Scott, B.F. and Nagy, E. 1982. Studies on the degradation of fate of TFM in the aquatic environment. A report to the Great Lakes Fishery Commission, Dec. 2, 1982.

5. Carey, J., Fox, M.E., Metcalfe, J.L., Brownlee, B., Macon, P. and Yerex, W.H. The fate and effects of contaminants in Canagagigue Creek. 1. Stream ecology and identity of major contaminants. IWD Scientific Series, #135, 1983.

6. Metcalfe, J.L., Fox, M.E. and Carey, J.H. 1984. Aquatic leeches (Hirudinea) as bio-indicators of organic chemical contaminants in freshwater Ecosystems. Chemosphere 13(1):143-150.

7. Carey, J.H., Fox, M.E., Brownlee, B.G., Metcalfe, J.L. and Platford, R.F. Disappearance kinetics of 2,4,- and 3,4-dichlorophenols in a fluvial system. Accepted by Can. J. Phys. and Pharmacol.

ORGANIC CONTAMINANT SOURCES IN THE GREAT LAKES BASIN

by

K.L.E. Kaiser, M.E. Comba and J.M. Ribo

INTRODUCTION

The Great Lakes are a valuable freshwater resource which is exposed to numerous industrial effluents carrying a multitude of known and unidentified contaminants. As a result, the availability of uncontaminated fish and water for human consumption is threatened. This study is part of a multidisciplinary effort to identify contaminants and to describe their sources, pathways and sinks in selected parts of the Great Lakes Basin.

RESEARCH RESULTS

In the past season, our research was centred on the Detroit River. In collaboration with several other studies, we pursued the identification and quantification of

(i) volatile halocarbons in water as descriptors of sources and physical movement within the river (refs. 1, 2);
(ii) polynuclear aromatic hydrocarbons, chlorinated benzenes, phenols and biphenyls (ref. 3) in water and sediments; and
(iii) contaminant sources by "in-situ" measurements of the toxicity of water to Photobacterium phosphoreum with the Microtox™ test (ref. 4).

The results indicate numerous inputs of chlorinated and volatile contaminants along the entire shore of the Detroit River. In particular, high levels of methylene chloride and tri- and tetrachloroethylene were observed at several locations, primarily on the right hand shore of the river (Fig. 1). In addition, three sampling stations were found to have highly toxic concentrations of as yet unidentified compounds. Further evaluations and identification is in progress at this time.

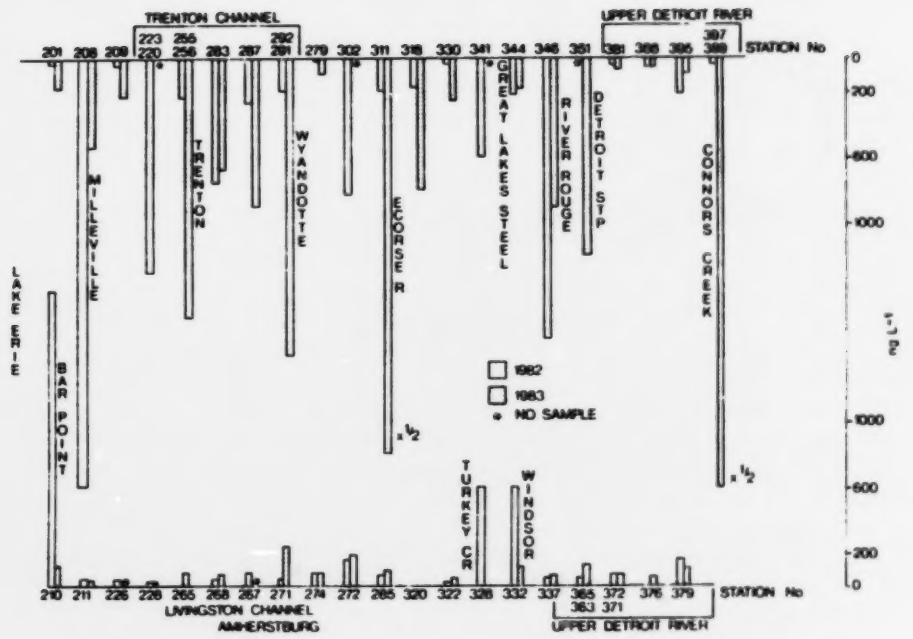

Figure 1. Industrial source volatile contaminant concentrations in nearshore water of the Detroit River (from ref. 2)

PUBLICATIONS

1. Comba, M.E. and Kaiser, K.L.E. Tracking river plumes with volatile halocarbon contaminants: The Niagara River-Lake Ontario example. J. Great Lakes Res. (in press).

2. Kaiser, K.L.E., Comba, M.E., Maguire, R.J., Tkacz, R.J. and Platford, R.F. Volatile halocarbons in the Detroit River and their relationships with other contaminants. J. Great Lakes Res. (in preparation).

3. Platford, R.F., Maguire, R.J., Tkacz, R.J., Kaiser, K.L.E. and Comba, M.E. Distribution of chlorinated hydrocarbons between the surface microlayer, subsurface water and sediment of the Detroit River. J. Great Lakes Res. (in preparation).

4. Ribo, J.M. and Kaiser, K.L.E. Microtox toxicity test results of water samples from the Detroit River area (in preparation).

AVAILABILITY OF ELEMENTS OF ENVIRONMENTAL IMPORTANCE

by

K.R. Lum

INTRODUCTION

The objective of this study is to develop and apply biogeochemical methods of investigating particle-mediated processes affecting the chemical composition of lakes and rivers and to evaluate the environmental impact of possible changes. In this study the impact of inorganic environmental substances is assessed by determining:

1) their availability, chemical speciation and distribution in the dissolved state
2) their mobility, modes of transport and chemical forms in suspended and bottom sediments.

RESEARCH RESULTS

Twenty surficial sediment samples from the Detroit River and Western Lake Erie have been analyzed for potentially available forms of sixteen elements. Apart from establishing the degree and extent of contamination of this system by these elements, the study has focussed on the geochemical factors controlling transport and availability of a number of elements of environmental significance. Adsorption equations have been calculated for eight elements associated with iron-oxides. The results show that these iron forms are effective scavengers of phosphorus and in the Detroit River-Lake Erie system exhibit a sorption capacity (on a molar basis) of 36.1%. This figure compares very well with that observed for phosphate removed from sea water on volcanogenic iron oxides at oceanic rises. Iron oxides are also important in the Detroit River as scavengers of Ni, Cr, Co, Zn and Mn (Lum and Gammon, 1984).

Work on suspended particulate matter in Lake Ontario and Hamilton Harbour shows the prevalence of cadmium in readily-available forms, Table 1 (Lum and Edgar, 1983). In a study of

TABLE 1. DISTRIBUTION OF THE CHEMICAL FORMS OF CADMIUM IN SUSPENDED SEDIMENTS FROM HAMILTON HARBOUR AND WESTERN LAKE ONTARIO

	Hamilton Harbour	Lake Ontario
Exchangeable forms, %	10 ± 3	17 ± 5
Carbonate and surface-oxide bound, %	18 ± 12	31 ± 10
Bound to Fe and Mn oxides, %	53 ± 8	34 ± 7
Bound to organic matter, %	7 ± 3	12 ± 5
Residual forms, %	12 ± 9	6 ± 3
Total cadmium concentration range,/$\mu g\ g^{-1}$	5.0-8.0	3.5-8.0

elemental cycling in the water column of the depositional area of the western basin of Lake Ontario, the proportion of phosphorus in readily-available forms decreases with depth indicating regeneration and recycling of phosphorus during sedimentation. In contrast, bottom sediments contain little or no readily-available phosphorus. For Lake Erie, phosphorus concentrations in suspended particulate matter are ca 0.2% whereas for the oxidized surface layer/top 1 to 2 cm of the bottom sediment, the concentrations are ca 1/3 those measured in suspended particulates.

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PARTICLE SIZE AND COMPOSITION EFFECT ON CONCENTRATION OF CONTAMINANTS IN LACUSTINE AND FLUVIAL SEDIMENTS

by

A. Mudroch

INTRODUCTION

There is considerable evidence in the scientific literature that contaminants such as metals and some organics can be taken up and concentrated by sediments and suspended matter in aquatic ecosystems. Many studies have shown that metal concentrations in the sediment depend on the granular composition of the material: higher concentrations are associated with the fine-grained sediment fraction. In the Great Lakes correlation was observed between sediment organic C and clay-size particles and between organic C and metal concentrations. However, these correlations were not found in the Niagara River sediment (1). Studies of morphology and chemistry of suspended matter in Lake Erie (2) indicated settling of large flocculates of organic matter and inorganic particles in the shallow water areas during lake stratification. The association of metals with sediment components, such as various minerals and organic matter plays an important role in their bioavailability.

The objective of the 1983/84 study was to characterize the sediment particles of different size, investigate their association with organic matter and metals and assess the bioavailability of metals in different types of sediments.

RESEARCH RESULTS

Concentration of major elements and metals (Zn, Cu, Cr, Ni, V, Co and Pb) and organic matter was determined together with mineralogical composition and particles morphology in eight size fractions (<2 μm to >250 μm) in the nearshore and offshore Lake Erie sediments. The investigation showed that the distribution of metals in the offshore sediment is bimodal with the majority of

metals divided between 63 to 250 µm size fraction which contains also highest concentration of organic matter, and the < 4 mm fraction composed mainly of clay minerals. However, metals in the nearshore sediment were associated mainly with the clay minerals (3).

Bioassays were carried out using elutriates from different types of sediment and natural phytoplankton population from the Great Lakes. The results indicated that nutrients (N and P) concentration affects the chemical forms of metals in the elutriates which, in turn, effect the phytoplankton population (4,5).

The effects of past mining activities on water and sediment quality was studied at the Shubenacadie headwater lakes in Nova Scotia. Study will continue in 1984/85. An investigation was carried out on the impact of abandoned landfill site on water, bottom sediments, soil strata and groundwater at the Durham Cruise Marina, Oshawa Harbour, Ontario. The availability of contaminants in selected sediment and soil samples was assessed by a bioassay procedure. It was found that the abandoned landfill site affects a large area including the Durham Cruise Marina. Results of the phytoplankton bioassays indicated some toxic effects of metals released during the elutriation of sediment and soil samples by lake water (6).

The effect of various concentrations of fulvic acid and $Ca(OH)_2$ on the chemical speciation of soluble metals in five Quebec lakes near the Noranda smelter was examined by the computer program "Geochem". The addition of fulvic acid did not affect the chemical speciation of Ca, Mg, Na, K, Fe and Al; however, Cu, Mn and Ni were associated with the organic part of the system in the water. Up to 91% of Cu and 15% of Ni were complexed by OH after addition of $Ca(OH)_2$ (7).

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CHEMISTRY OF CHLORINATED HYDROCARBONS AT THE AIR/WATER INTERFACE

by

R.F. Platford and R.J. Maguire

INTRODUCTION

The Division conducted a comprehensive sampling program on the Detroit River in 1983.

RESEARCH RESULTS

Our large volume APLE water sample has been tested and used in the field. Our microlayer sampler has been built and tested on the Niagara River. Halogenated hydrocarbons (chlorobenzenes and PCBs) and polyaromatic hydrocarbons (PAHs) were detected in the surface microlayer, the subsurface water the suspended solids, the sediments and the pore water in the sediments. The concentrations of the chlorinated hydrocarbons were from 10-1000 times higher in the surface microlayer than in the subsurface water, and were up to 10^5 times higher in the sediments and suspended solids than in the subsurface water (Figure 1). The top 10 cm of sediment contained more than 99% of the chlorinated compounds we detected in the river system.

The PAHs were not as strongly partitioned as the chlorinated compounds, and a significant fraction resided in the subsurface water and pore water.

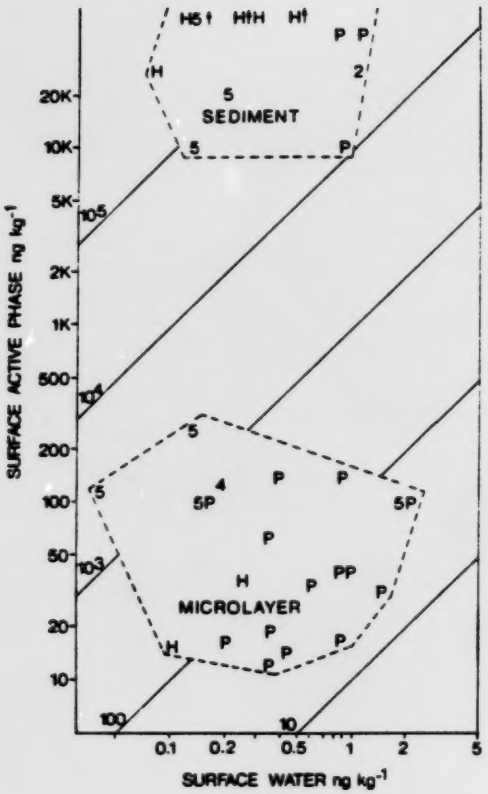

Figure 1. Enhancement of concentration of chlorinated benzenes in solid and microlayer phases in the Detroit River during the summer of 1983.

Key:
- 2 1,2 Dichlorobenzene
- 4 1,2,4,5, Tetrachlorobenzene
- 5 Pentachlorobenzene
- H Hexachlorobenzene
- P Polychlorinated Biphenyls

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RADIONUCLIDE PATHWAYS IN THE NIAGARA RIVER

by

S.R. Joshi and S.P. Thompson

INTRODUCTION

Nuclear fuel reprocessing activites at NFS, Inc., located 65 km upstream of Lake Erie (in West Valley, NY, U.S.A.) started in 1966. Though the NFS ceased fuel reprocessing in 1972, storing of spent fuel continued until 1976. Evidence of former reprocessing activities at West Valley has been found in sediment and fish samples from the Cattaraugus Creek. Limited amount of available data suggests that very low levels of transuranium isotopes are reaching the receiving Lake Erie waters. The present study was initiated to determine the inputs, if any, of these radionuclides to Lake Ontario via the Niagara River. Initially it was planned to measure only the $^{239,240}Pu$ profiles in ^{210}Pb-dated Lake Ontario sediments. Various isotopes of uranium and thorium as well as ^{241}Am and other gamma-emitting radionuclides were subsequently added to the investigations.

RESEARCH RESULTS

The measurement of these radionuclides in sediment required the availability of a reliable method for their simultaneous determination at extremely low levels. A literature survey revealed that no simple method is available for this purpose. Experiments were, therefore, initiated to evaluate the existing few procedures. These experiments have resulted in the development of procedures for the measurement of $^{238,239,240}Pu$, ^{241}Am, ^{210}Pb, $^{228,230,232}Th$, ^{226}Ra, and $^{234,235,238}U$ using the same subsample. These procedures involve the leaching of all isotopes with hot, concentrated HNO_3 following spiking with ^{242}Pu and gamma-ray spectrometry. Various Th, U and Pu isotopes are then separated and purified using an anion-exchange technique. Individual isotopic contributions are

then determined either by alpha-particle spectrometry of the separated isotopes or by the combined use of alpha-particle and gamma-ray spectrometric measurements.

A lanthanum fluoride coprecipitation technique has replaced the conventional, time-consuming electrodeposition technique for preparing sources for alpha-particle spectrometry. Typical alpha-particle spectra of radionuclides isolated from a Lake Ontario sediment sample are shown in Figure 1. The entire

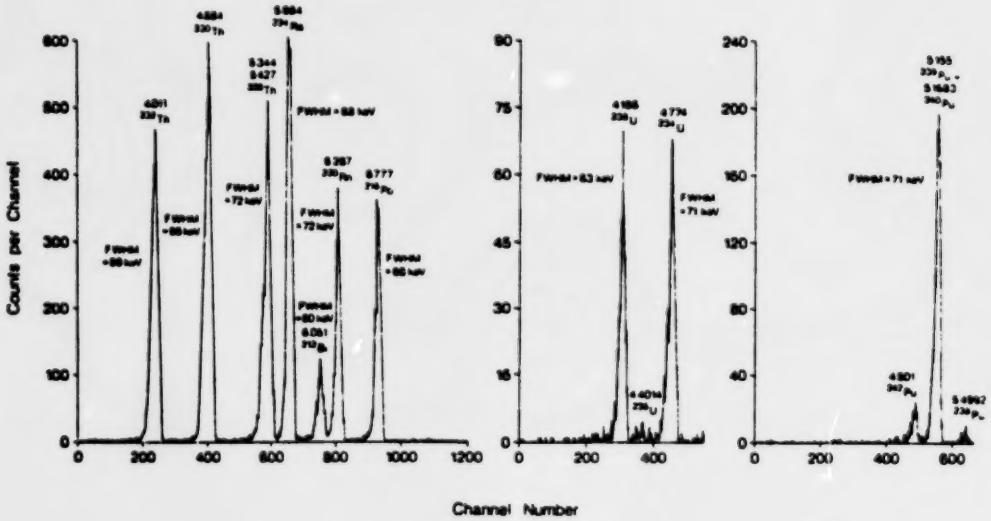

Figure 1. Alpha-particle spectra of actinides isolated from a Lake Ontario sediment sample. Energies in MeV.

wet chemical procedure can be completed in about two days, while the gamma- and alpha-measurements required 4 to 8 days per sample (depending upon the number of radiation detectors used) for all radioisotopes mentioned earlier.

The application of these procedures to the determination of radionuclide levels in sediment cores collected from five locations in Lake Ontario commenced in March 1983. So far over 50 samples, representing top 10 cm in each core, have been gamma counted and chemically processed for the isolation of actinides. An integral part of this study involved determination of sedimentation rates by the ^{210}Pb method. These measurements

; the rates at study locations are generally higher than ıred previously for other locations in the Great Lakes Lake Ontario. The rates vary between 0.2 and r^{-1} (74.2 to 487.8 mg cm^{-2} yr^{-1}). The flux of : ^{210}Pb at the sediment/water interface varies between).12 Bq cm^{-2} yr^{-1}, while the sediment porosity ranges 83 and 0.92. These data will be used to assess the artificially-produced radionuclides to western Lake diments. In addition, the study will also provide ı on the levels of various Th and U isotopes.

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B. PRIMARILY PROJECTS RELATED TO TOXIC CONTAMINANTS IN THE GREAT LAKES IN GENERAL AND FATE OF TOXIC METALS, ORGANOMETALLICS, RADIONUCLIDES AND CHLORINATED ORGANICS.

SOURCES, SPECIATION AND CONCENTRATION OF ORGANOTIN AND ORGANOLEAD IN THE ENVIRONMENT

by

Y.K. Chau, G.A. Bengert, P.T.S. Wong and A.J. Carty

INTRODUCTION

The widespread of organotin and organolead compounds in environmental samples as a result of their extensive use has warranted several studies within the Division with regard to their environmental formation, occurrence (7,8) and toxicity (4). Recent finding of high concentrations of different alkyllead species (R = Me, Et) in fish and macrophytes (7) in areas related to production of tetraalkyllead necessitates the need to study their transformation and degradation in the aquatic systems.

RESEARCH RESULTS

Preliminary results indicated that transmethylation reactions between methyllead and inorganic tin (II) occurs. These reactions are enhanced in sediment matrix suggesting possible biological mediation.

$$Me_3Pb^+ + Sn\ (II) \rightleftharpoons Me_nSn^{(4-n)+}$$

A fish digestion technique using a tissue solubilizer, Tetramethylammonium hydroxide (TMAH) has been developed to dissolve fish tissues without breaking down the organometallic compounds (7). With this technique, the various alkyllead species can be determined for the first time simulataneously in fish and biological samples.

Two field trips were completed in Detroit, St. Clair rivers and Maitland, St. Lawrence River areas. Analyses of surface microlayer and surface water samples showed significant concentrations of dialkyllead and trialkyllead and tetraethyllead. Sampling will continue this year to study the

distributions of different species in relation to their relative stability under environmental conditions.

Analysis of fish samples from Maitland, St. Lawrence river area showed serious contamination of alklyllead compounds. The amjor alkyllead species found in fish and sediment were tetraethyllead and its degradation products, triethyllead. diethyllead and lead (II). A sampling program in collaboration with Great Lakes Fisheries Research Branch will be carried in the coming field season.

A study of the environmental occurrence and concentration of organotin compounds under a GLWQP contract has been completed. Methyltin and butyltin compounds were present in harbors and heavily industrialized areas associated with organotin usage. A NWRI report has been prepared in collaboration with R.J. Maguire and P.T.S. Wong (8).

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TRENDS IN RADIOACTIVE CONTAMINANTS OF THE GREAT LAKES

by

S.R. Joshi and S.P. Thompson

INTRODUCTION

Radioactivity levels in the Great Lakes are a concern for most of the 30 million people in the Basin who get their drinking water from the Great Lakes. Inputs come from weapons testing fallout and operation of the nuclear fuel cycle in the Great Lakes Basin. Currently there is 14.8 GW of installed electrical generating capacity on the shores of Lakes Michigan, Huron, Erie and Ontario, with an equivalent amount in the construction phase. Uranium mining and milling operations are carried out at Port Hope on the north shore of Lake Ontario with wastes being landfilled at nearby Port Granby. These wastes are leached through groundwater to the lake. Water and fish samples are collected annually from the lakes and radionuclide concentrations measured in order to determine trends, radiological dose to the population and bioaccumulation factors for fish.

RESEARCH RESULTS

All the Great Lakes were sampled during 1983 at three stations in each lake. Fifty litre water samples were collected at the surface and near the bottom at each station and must have been analysed for ^{3}H, ^{90}Sr, ^{137}Cs, ^{125}Sb, and total U. Results of the analyses of the 1982 sampling programme were published during 1983. The mean values of radionuclide concentrations for each lake are given in Table 1. The values show little change from those for 1980 and 1981, except that ^{3}H is highest in Lake Erie than in Lake Ontario where continuous releases of ^{3}H are taking place.

The radiological dose to invidivuals drinking Great Lakes water is essentially all due to fallout ^{90}Sr. The annual

dose commitments calculated from the ^{90}Sr concentration for 1982 were Lake Superior - 0.06 mrem, Lake Huron - 0.11 mrem, Lake Erie - 0.095 mrem, and Lake Ontario - 0.12 mrem. These values are all less than the 1 mrem water quality objective for radioactivity in the Great Lakes Water Quality Agreement of 1978.

TABLE 1. MEAN RADIONUCLIDE CONCENTRATIONS IN THE GREAT LAKES

Lake	Concentration in $pCiL^{-1}$				
	^{3}H	^{137}Cs	^{125}Sb	^{90}Sr	U(μgL^{-1})
Superior	145±68	0.045±0.004	0.012	0.41±0.03	0.08±0.01
Huron	247±100	0.031±0.006	0.014	0.73±0.06	0.39±0.05
Erie	328±28	0.015±0.003	0.016±0.006	0.63±0.04	0.59±0.04
Ontario	235±12	0.29±0.003	0.015±0.006	0.79±0.05	0.42±0.03

Bioaccumulation of radionuclides in fish was also determined. The highest value for ^{137}Cs, 7200, was found for lake trout from the North Channel of Lake Huron. The average bioaccumulation factor for rainbow trout, lake trout, and walleye at other locations was about 1500 for ^{137}Cs. The concentrations of ^{226}Ra in these fish were low. The measured values are given in Table 2.

TABLE 2. RADIONUCLIDE CONCENTRATIONS IN GREAT LAKES FISH

			Mass of Whole Fish kg	Concentration in Fresh Fish ($pCiKg^{-1}$)	
				^{137}Cs	^{226}Ra
Ontario	Cobourg	Rainbow Trout	3.44	41±3	0.4±0.2
		Lake Trout	2.58	44±3	0.2
		Lake Trout	2.25	41±3	0.2
		Lake Trout	1.96	39±3	0.3±0.1
	Niagara-on-the-Lake	Lake Trout	2.22	51±5	0.7±0.2
		Lake Trout	1.18	34±2	0.4±0.2
		Lake Trout	2.86	45±3	0.7±0.2
		Lake Trout	1.95	33±3	0.2
Huron	North Channel	Lake Trout	3.91	217±5	0.5±0.3
		Lake Trout	2.19	214±4	0.2
		Lake Trout	2.59	236±5	0.6±0.2
Erie	West Basin	Walleye	1.97	28±3	1.2±0.2
		Walleye	1.63	18±2	1.1±0.2
		Walleye	2.24	24±2	1.9±0.2

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FATE OF ORGANOTINS IN WATER

by

R.J. Maguire, R.J. Tkacz and D.L. Sartor

INTRODUCTION

Organotin compounds are used in three main ways, viz., as stabilizers for polyvinyl chloride, as catalysts in the production of polyurethane foams, and as biocides. The increasing annual use of organotin compounds raises the possibility of environmental pollution. Organotin compounds are a chemical class about which more information is sought under Canada's Environmental Contaminants Act regarding toxicology and environmental fate. Our work has concentrated on the aquatic persistence and fate of the tri-n-butyltin species (Bu_3SN^+), which, in various compounds, is used in antifouling paint formulations for ships and docks, as a general lumber preservative, and as a slimicide in cooling towers. We have detected the Bu_3Sn^+, Bu_2Sn^{2+} and $BuSn^{3+}$ species in some waters and sediments in Ontario. The Bu_3Sn^+ species is of most concern since the toxicity of alkyltin species declines dramatically with decreasing number of alkyl groups. Our earlier determination of some physical and chemical characteristics of the Bu_3Sn^+ species indicated that it may be moderately persistent in water. Bu_3Sn^+ dissolved in water neither volatilizes nor loses butyl groups over a period of at least two months in the dark at 20°C; in sunlight, however, it undergoes slow (half-life greater than 89 d) photolytic degradation, at least partially by stepwise debutylation to inorganic tin. Work remaining to be done in this study is (i) algal, bacterial and fish uptake and metabolism of Bu_3Sn^+, (ii) persistence and fate of Bu_3Sn^+ in a sediment-water mixture, and (iii) a cross-Canada survey for butyltin compounds in water, sediment and fish.

RESEARCH RESULTS

The accumulation and metabolism of Bu_3Sn^+ by a green alga, Ankistrodesmus falcatus, was determined at 20°C over a 4-week period; about 50% of the original Bu_3Sn^+ was converted to Bu_2Sn^{2+} and small quantities of $BuSn^{3+}$ and inorganic tin. An apparent algal bioconcentration factor of 3×10^4 was estimated for Bu_3Sn^+.

A preliminary report was written on a survey to determine the extent of contamination of waters on the Canadian side of the Great Lakes basin by methyltin and butyltin compounds. About 100 locations were sampled. Butyltin species were widely found in water and sediment samples. The highest concentrations were in harbours, reflecting the use of tributyltin compounds as antifouling agents in boat paint. Methyltin species were infrequently detected, and their occurrence was correlated with the presence of relatively high concentrations of inorganic tin.

A review was written of the analysis, occurrence and fate of organotin compounds in the environment. The main conclusions were:

(a) The state of the art in analytical instrumentation is generally adequate, although there are few published methods on media other than water. The main classes of organotin compounds likely to be found in the Canadian environment are methyl-, butyl-, octyl-, phenyl- and cyclohexyltin compounds, and most of these species can be analyzed satisfactorily using existing methods; however, it is desirable to have a method which features continuous introduction of high pressure liquid chromatographic eluent into a suitable detector for those compounds, or conjugates, which are not volatile.

(b) There are few data on the occurrence of organotin compounds in the environment. Some of those that have been detected are very toxic to aquatic organisms.

(c) Persistence studies on the major classes of organotin compounds have indicated that abiotic degradation generally occurs, as does biological degradation, through mechanisms of sequential dealkylation or dearylation. Adsorption to soils and sediments appears to be strong, although subsequent mobilization by biota cannot be ruled out. In general, photolysis appears to be the rate-limiting degradative step. Methylation of tin and organotin compounds, although a slow

process, may nevertheless be significant with regard to transport of tin in and from aquatic environments.

Work is in progress on (i) trout uptake and metabolism of Bu_3Sn^+, and (ii) the persistence and fate of Bu_3Sn^+ in a sediment-water mixture. In FY 84/85 work will concentrate on bacterial metabolism of Bu_3Sn^+ and a cross-Canada survey for butyltin compounds in water, sediment and fish.

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CHLORINATED HYDROCARBONS IN WATER, SEDIMENTS AND BIOTA OF THE GREAT LAKES

by

B.G. Oliver and K.D. Nicol

INTRODUCTION

The contamination of the Great Lakes with persistent toxic organic chemicals is a problem of increasing public concern. The object of this project is to quantify organic pollutants in all compartments of the aquatic environment (water, sediment, biota), so compounds that are causing or could cause problems are identified. From this type of compartmental analysis, pathways of the contaminants in the aquatic environment can be traced and correlated with the compound's physical and chemical properties. Such structure-behavior correlations are important since we do not have the resources to study individually all potential problem chemicals.

RESEARCH RESULTS

Work on chlorinated contaminants in the Niagara River and adjacent Lake Ontario is continuing (1-5). A two-year study on 31 chlorinated compounds in weekly samples from the river at Niagara-on-the-Lake was recently completed (4). The study showed a measureable background concentration for most contaminants in the river, likely due to steady leaching from chemical waste disposal sites along the river. Superimposed on this background were large unpatterned concentration spikes due to direct chemical discharges to the river. Although some reduction in discharges has been achieved in recent years (1), this study shows that chemical dumping into the river still is a problem.

The river contaminants adsorbed to settling particles in Lake Ontario have been studied using sediment traps (5). Contaminant fluxes to the lake sediments were found to be much lower than anticipated likely due to significant volatilization losses from

the lake. The trace organic composition of sediment trap material revealed that considerable resuspension of bottom sediments is occurring in Lake Ontario particularly during the winter months.

Studies on the uptake and elimination of contaminants by rainbow trout (with A. Niimi, GLFRB) are continuing (6-9). The bioconcentration factors determined in these studies have been related to physical-chemical properties of the chemicals. The correlation is good for small compounds with low octanol-water partition coefficients ($<10^5$), but breaks down for large molecules with high partition coefficients.

PUBLICATIONS

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2. Fox, M.E., Carey, J.H. and Oliver, B.G. 1983. Compartmental distribution of organochlorine contaminants in the Niagara River and the Western Basin of Lake Ontario. J. Great Lakes Res. (Niagara River Symposium issue) 9:287.

3. Oliver, B.G. and Nicol, K.D. 1983. Comment on chlorobenzenes in sediments, water and selected fish from Lake Superior, Huron, Erie and Ontario. Environ. Sci. Technol. 17:504.

4. Oliver, B.G. and Nicol, K.D. 1984. Chlorinated contaminants in the Niagara River, 1981 to 1983. Sci. Total Environ. (in press).

5. Oliver, B.G. and Charlton, M.N. 1984. Chlorinated organic contaminants on settling particulates in the Niagara River vicinity of Lake Ontario. Environ. Sci. Technol. (in press).

6. Oliver, B.G. and Niimi, A.J. 1983. Bioconcentration of chlorobenzenes from water by Rainbow Trout: correlations with partition coefficients and environmental residues. Environ. Sci. Technol. 17:287.

7. Niimi, A.J. and Oliver, B.G. 1983. Biological half-lives of polychlorinated biphenyl (PCB) congeners in whole fish and muscle of Rainbow Trout (Salmo gairdneri). Can. J. Fish. Aquat. Sci. 40:1388.

8. Oliver, B.G. And Niimi, A.J. 1984. Rainbow trout bioconcentration of some halogenated aromatics from water at environmental concentrations. Environ. Toxicol. Chem. (in press).

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ENVIRONMENTAL DISTRIBUTION OF TOXIC CHEMICALS

by

W.M.J. Strachan

INTRODUCTION

The environmental assessment of chemicals requires an understanding of the distribution which these substances assume once they are released to the environment. It is a truism that assessment questions are being and will continue to be asked about chemicals for which no field data exists. As part of a project to be able to predict distributions, this study is attempting to evaluate some computer models of a variety of scenarios and to gather necessary data to validate and/or verify the predictions.

RESEARCH RESULTS

During FY 1983-84, three models which describe the environmental distribution of chemicals were examined. The EXAMS model (Lassiter and Burns, EPA, Athens, Ga.), FUGACITY (D. Mackay, University of Toronto), and PERSISTENCE (J.R. Roberts, NRC, Ottawa) were investigated for conversion to microcomputer format and it is expected that copies of the reports investigated for conversion will be generally available shortly. In addition, a sensitivity analysis (single variant) of predicted outputs as a function of input values was undertaken; most chemical and some system input parameters were varied by 100% to determine the impact on the predicted compartmental concentrations. An internal report is in preparation.

Sound statistical data for different parameters are required to evaluate the predictions from models such as the preceding. Triplicate rain samples were collected from two Lake Superior sites (Isle Royale, USA, and Caribou Island, Canada) and mean values are presented in Tables 1a and 1b.

TABLE 1a. RAIN DATA FROM CARIBOU ISLAND, LAKE SUPERIOR, 1983. (FIGURES ARE IN ng/L)

Compound*	April 21 - May 22	May 22 - July 10	July 10 - Sept 5	Sept 5 - Oct 10	Oct 10 - Nov 22
α-BHC	9.2	46.0	3.9	5.8	4.6
Lindane p.	4.2	12.0	1.6	1.8	1.6
Heptachlor ep.	0.5	0.6	0.1	nd	0.1
Dieldrin	0.7	nd	0.3	0.2	0.3
Endrin	nd	nd	nd	0.09**	nd
pp'-DDE	1.0	nd	0.02	nd	nd
pp'-DDT	nd	0.2	0.2	0.2	0.1
pp'-DDD	nd	nd	nd	0.05**	0.03
Methoxychlor	3.3	4.1	0.4	2.6	1.4
PCBs	48.0	6.1	0.6	2.0**	2.1
HCB	nd	0.1	0.02	0.4**	nd
Rain (L)	7.9	26.3	33.6	19.7	21.7
(mm)	38.0	126.0	161.0	94.0	104.0

*Other compounds looked for but not found above detection levels (noted in ng) were: toxaphen (5); op'-DDT (0.4); α- and β-chlordane (1.0 ea) and mirex (0.4).
**Duplicate samples only.

TABLE 1b. RAIN DATA FOR ISLE ROYALE, LAKE SUPERIOR, 1983. (FIGURES ARE IN ng/L)

Compounds*	May 19 - July 2	July 2 - Sept 4	Sept 4 - Oct 15
α-BHC	65.0	40.0	19.0
Lindane	16.0	8.2	4.6
Heptachlor ep.	1.3	nd	0.4
Dieldrin	nd	1.3	0.6
Endrin	nd	nd	0.3
pp'-DDE	nd	0.7	nd
pp'-DDT	0.1	nd	nd
pp'-DDD	nd	nd	0.5
Methoxychlor	7.4	1.5	1.3
PCBs	16.0	5.4	1.4
HCB	0.1	0.01	nd
Rain (L)	17.6	17.1	34.5
(mm)	84.0	82.0	165.0

*Other compounds looked for but not found above detection levels (noted in ng) were: toxaphen (5); op'-DT (0.4); a- and β-chlordane (1.0 ea); and mirex (0.4).

A literature investigation into appropriate components of a laboratory model ecosystem was also undertaken. A simple stream ecosystem is being considered as well as a static, purely abiotic system. Both are intended primarily to measure concentrations in important compartments of systems at equilibrium or steady state.

PUBLICATIONS

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2. Strachan, W.M.J. and Huneault, H. 1983. Evaluation of an organic automated rain sampler. Environ. Canada, Inland Waters Directorate Technical Bulletin 128.

3. Strachan, W.M.J. and Edwards, C.J. 1983. Organic pollutants in Lake Ontario. in Toxic Contaminants in the Great Lakes. ed. J.O. Nriagu, M.S. Simons, J. Wiley, N.Y. (in press).

RADIUM PATHWAYS FROM PORT GRANBY WASTE MANAGEMENT SITE TO LAKE ONTARIO

by

R.F. Platford, A.B. Bobba, S.R. Joshi and J.A. FitzGerald

INTRODUCTION

The radionuclides section continues to monitor the transport of refining waste from the Port Granby site to Lake Ontario.

The concentrations of radium-226 and of natural uranium have been measured over the period from 1981 to 1983 in the groundwater along the shore of the site; the results have been used to develop a two-dimensional transport model for the area.

RESEARCH RESULTS

A total of about one thousand groundwater samples have been collected from the shore of the Port Granby site from 1981 to 1983 and were analyzed for radium-226 (about 600 samples) and uranium (about 400 samples). The radium-226 activites at seven of the 50 sampling sites were as much as ten times higher than the Ontario drinking water standards. The uranium concentrations at 15 sites were as much as 50 times higher than the Ontario drinking water standards; however, the uranium standard is probably too low at present and may be revised upward. Work in previous years indicates that there is a dilution of the contamination by at least a factor of ten, and that the Ontario drinking water standards are met once one moves more than a few metres offshore of the site.

PUBLICATIONS

1. Platford, R.F., FitzGerald, J.A., Bobba, A.G. and Joshi, S.R. 1984. Report on the groundwater at the Port Granby Radioactive Waste Management Site from 1981 to 1983. NWRI Report No. 84-9.

C. PROJECTS DEALING PRIMARILY WITH THE FATE OF TOXIC METALS AND ORGANIC CHEMICALS IN FLUVIAL ECOSYSTEMS OTHER THAN THE GREAT LAKES

ACCUMULATION/DEGRADATION OF ORGANIC CONTAMINANTS IN FLUVIAL SYSTEMS

by

J.H. Carey, M.E. Fox, J.L. Metcalfe and P.A. Coletta

INTRODUCTION

Investigations into the behaviour of contaminants in polluted locations are needed as a complement to laboratory investigations of the contaminant properties. In this study, laboratory investigations of the pathways of degradation and accumulation of contaminants are coupled with field work at locations across Canada.

RESEARCH RESULTS

At Canagagigue Creek, work on the accumulation and degradation of benzothiazoles and chlorophenols has continued. A detailed study of the disappearance kinetics was performed. The results indicate that, once allowance is made for the effect of streamflow on transit times, the disappearance rate of 2,4- and 3,4-dichlorophenol from Canagagigue do not show a significant seasonal variation from April (just after spring runoff ends) to December (just before freeze-up). We interpret these results as an indication of the importance of degradation within the periphytic biofilm covering the stream bottom. A paper was prepared on the subject. With the aid of S. Painter and J. Wood of AED, an expanded macrophyte and periphyton survey was conducted. The samples are being analysed for chlorophenols and benzothiazoles in an attempt to document the unexpected accumulation patterns observed in 1982.

The route of formation of the oxygen containing MMBT derivatives remains unknown. An examination of the wastewater from mercaptobenzothiazole synthesis supplied by Uniroyal Chemicals revealed that neither MMBT nor the oxidised derivatives were present. An examination of water from the Uniroyal waste

lagoons also failed to detect these compounds. We now speculate that these compounds arise in the Water Pollution Control Plant from non-chromatographable precursors. Work on identifying the precursors will continue.

A gel permeation chromatographic method for lipid clean-up of samples was set up and characterized. The method was used in the removal of lipids from extracts of tissues from Old Squaw ducks from the Niagara River. The extracts were analysed for neutral organochlorine compounds and for chlorophenols. A linear correlation was observed between the concentrations of the major contaminants in each duck. Since several of these contaminants (e.g., mirex) are virtually unique to the Niagara/Lake Ontario system, we interpret these results as indicating that most of the contaminants in these ducks were obtained while they wintered on Lake Ontario. A full report is in preparation.

Several sets of samples from the North Saskatchewan and Qu'Appelle systems were obtained and extracted. Work done by our collaborators in EPS, Edmonton showed that the gel permeation clean-up method was subject to some interference which caused the loss of some chlorophenols and other acidic compounds. Until this problem is resolved, the clean-up of the western samples is suspended.

Work on the photodegradation of contaminants in streams has centered on the production of reactive species in the indirect photolysis of water containing humic acids and also on the route of TFM photodegradation. Superoxide was found to be produced when two filter-sterilized waters were exposed to sunlight and a paper was published on this subject. With respect to TFM, a field study has confirmed that the direct photolysis of this compound can occur in a stream during treatment and a second study, performed in collaboration with E. Nagy and B. Scott, has shown that the half-life of TFM in experimental ponds was in agreement with our previous predictions.

PUBLICATIONS

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2. Carey, J., Fox, M., Brownlee, B., Metcalfe, J. and Platford, R. 1984. Disappearance of chlorophenols in a fluvial system. Submitted to Can. J. Phys. and Pharmacol.

3. Scott, B., Carey, J., Nagy, E. and Dermott, R. 1984. The fate of TFM in quiescent waters and its impact on benthos. Submitted to Can. J. Water Poll. Res.

ACCUMULATION AND EFFECTS OF CONTAMINANTS IN AQUATIC BIOTA

by

J.L. Metcalfe, J.H. Carey, M.E. Fox, P.A. Coletta,
D.R. Barton and J. Madill

INTRODUCTION

This study is a part of the Canagagiue Creek Project in which the fate and effects of organic contaminants, including chlorophenols, benzothiazoles, and lindane are under investigation. Two types of studies are being conducted. They are studies aimed at establishing the potential of leeches as bioindicators of contaminants in freshwater systems, and studies to determine the pathways and accumulation rates of organic contaminants in fish.

RESEARCH RESULTS

Chlorophenol analyses were completed on the benthic invertebrate samples collected from Canagagigue Creek in 1981. Representatives of 3 phyla, 5 classes and 24 families of invertebrates had been obtained. Annelids (leeches and worms) accumulated the highest levels of CPs, these being from one to several orders of magnitude greater than the levels found in other benthos. Concentrations in leeches frequently reached the ppm level, with a maximum value of 15 ppm. Intermediate, but much lower, levels were found in the caddisfly Pycnopsyche and some Odonata (maximum 0.5 ppm). Molluscs contained the lowest concentrations of CPs with a maximum of 0.08 ppm.

Analyses were completed on samples of leeches and water collected from five sites in southwestern New Brunswick in 1982. Leeches were found to be good indicators of relative chlorophenol contamination in the water. They accumulated chlorophenols to levels 1100X to 130,000X those in the water, with major differences in bioaccumulation capacity among the various species. Only 3 chlorophenols were detected in the water, but a total of 12

were identified in leeches from various sites. Thus, leeches may be used to identify compounds present in the water at levels too low to be detected in conventionally-collected water samples.

A survey of organic contaminant levels in aquatic leeches from the Grand River watershed was conducted in 1982. At present chlorophenol determinations have been completed for 75% of these samples. Preliminary analysis of the data reveals that concentrations of CPs in leeches tend to increase as we proceed downstream (Table 1A). The first major source of chlorophenol contamination in the river is site GR-12 just below the mouth of Canagagigue Creek. In order to adequately compare sites, however, seasonal effects and differences in the bioaccumulation capacities of the various leech species will have to be taken into account. Four tributaries of the Grand River were also sampled, and the data are presented in Table 1B. As expected, the Speed River which flows through the cities of Guelph and Cambridge was the most contaminated.

A study of the influence of food chains on the uptake of chlorophenols and benzothiazoles by Canagagigue Creek fish was initiated this year. A total of 74 fish, representing 10 species, were collected from site CN-3 in May, and 108 fish, representing 8 species, were obtained in September. Organs (gonads, liver, gall bladder, spleen and kidneys) were removed for separate contaminant analyses and stomach contents were preserved for determining food habits. Probable food items and water samples were also collected. Significant seasonal shifts in the diets of most species were apparent. Fish collected in the spring tend to prey heavily on blackfly larvae with midge larvae next in importance, followed by leeches. Fish collected in the fall relied less heavily on blackfly larvae and leeches, but utilized damselfly larvae, water boatmen and plants much more significantly. These changes in diet reflected changes in the benthic community over the same time period, indicating that most species of fish are very opportunistic in their food habits.

An experiment to determine the uptake rates and accumulation plateaus for chlorophenols, benzothiazoles and lindane in several indigenous species of biota from Canagagiue Creek was conducted in August. Crayfish, common shiners and longnose dace were exposed on-site at CN-3. Contaminant analyses are forthcoming.

TABLE 1A. Average Total Chlorophenol Concentrations in Leeches from the Grand River; all Species and Seasons Combined

Site	Description	# Samples	Average Total Chlorophenol Concentration	Range of Concentrations
GR-2	Monticello	8	238 ng/g	26 - 661 ng/g
GR-7	Bellwood	13	214	37 - 448
GR-13	Elora	13	395	33 - 1081
GR-12	Below Elmira	14	1096	23 - 3392
GR-16	Glen Morris	7	1144	566 - 2165
GR-18A	Brantford	5	1118	414 - 1800
GR-19A	York	2	3450	1431 + 5468
GR-20	Dunnville	1	1340	-

NOTE: Sites are arranged in order from the furthest upstream (GR-2) to the furthest downstream (GR-20).

TABLE 1B. Average Total Chlorophenol Concentrations in Leeches from Tributaries of the Grand River; all Species and Seasons Combined

Site	Description	# Samples	Average Total Chlorophenol Concentration	Range of Concentrations
GR-14	Conestogo R.	8	870 ng/g	139 - 1817 ng/g
GR-15	Speed R.	12	1687	194 - 5528
GR-17A	Nith R.	4	1517	70 - 3622
GR-19	McKenzie Ck.	4	319	88 - 616

PUBLICATIONS

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3. Barton, D.R. and Metcalfe, J.L. Life histories and food habits of three species of freshwater leeches (Hirudinea) from Canagagigue Creek, Ontario. (In preparation for submission to Can. J. Zool.).

PERSISTENCE OF 2,4-D IN A NATURAL WATER SYSTEM

by

E. Nagy, B.F. Scott, S. Painter, J. Hart and J. Wood

INTRODUCTION

The growth of Eurasian milfoil in the Trent water system has been controlled for some years by the application of herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D). Our survey in the summer of 1983 was conducted to look for possible accumulation of this chemical in Buckhorn Lake sediments. In addition to the survey, an experimental herbicide application was made in a protected channel in Scollard Bay, to monitor its persistence and its spreading into the adjacent water body.

RESEARCH RESULTS

A survey of Buckhorn Lake sediment cores in May 1983 revealed the presence of 2,4-D in the top 30 to 50 cm of the sediment. The highest concentration of 0.84 mg/g was found in one of the previously treated areas. Sediment cores collected along a transect from the south shore into the lake showed diminishing concentrations, but 2,4-D was still detectable (about 10 micrograms/g) 2.8 km from the shore. These results indicated a significant level of persistence of the chemical from the previous year(s). Although mid-depth concentrations were higher in most cores, the chemical's distribution was fairly homogeneous in the sediment column, suggesting effective mixing. The extent of the survey is illustrated in Figure 1.

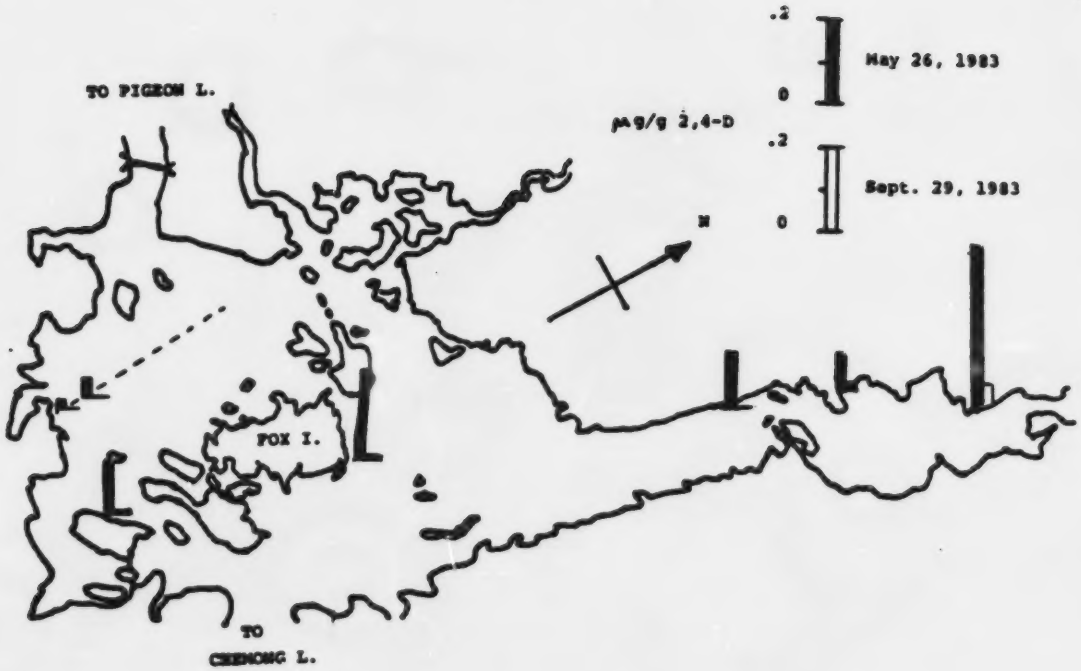

Figure. 2,4-D in Buckhorn Lake Sediments

The sur was repeated at the end of September, with surficial sedime samples taken from all previously sampled locations. The 2,4-D concentrations in all of these samples were much lower than tMay values. This suggested that the unusually warm summer prodd high degradation rates which had effectively removed most ofhe new chemical input from the 1983 summer applications.

The eimental 2,4-D application in Scollard Bay was overwhelmed by 2,4-D inputs elsewhere in the Bay. Water and sediment samplecollected in and near the treated channel in a 10-week periodicated current-dependent transport of the chemical in thele area.

Weller samples collected near the experimental site in early Augusl contained traces of 2,4-D (4.5 ppb maximum), suggesting greater transport of the chemical, By the end of August, the cal could not be detected in the same well waters.

Our plans for the 1984 field season call for an extensive survey, conducted weekly during the herbicide application period, to investigate possible lake-wide movements of the chemical.

PUBLICATIONS

Scott, B.F., Nagy, E., Dutka, B.J., Sherry, J.P., Taylor, W.D., Glooschenko, V., Wade, P.J. and Hart, J. 1984. The fate and impact of oil and oil-dispersant mixtures in freshwater pond ecosystems: Introduction. Science of the Total Env. 35, 105-114.

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AQUATIC IAYS OF RADIONUCLIDES RELEASED BY URANIUM MINING

by

S.R. Josh.F. Platford, J.A. FitzGerald and S.P. Thompson

INTRODUCTION

Nea 120 million tonnes of uranium mine and mill tailings, covng some 10 sq.km. and representing about 2% of all mine wastes Canada, exist in seven general areas in Ontario, Saskatchewan a NWT. Several tailings piles amounting to about 8 million tonne of tailings have been abandoned entirely in Saskatchewn (Gnr and Lorado) and NWT (Port Radium). There is little or no fomation available as to the levels and pathways of U-series radonclides which may be (or are being) released to the nearby wate odies. Such information is required to assess the current imac of radionuclide releases on local aquatic ecosystems and to construct a field measurement data bank for developing and erfying models designed to predict the long-term impact of such rleases. The title project was launched in 1983/84 to derive information for the above-mentioned purposes. The study areas hosen were Langley Bay/Lake Athabasca in Saskatchewan and Georgian Bay. The former site receives the run-off from the abandoned tailings of the former Gunnar uranium mine, while the latter site constitutes major water body in the vicinity of the Elliot Lake uranium mining areas.

RESEARCH RESULTS

Four sediment cores from various locations in Georgian Bay (Fig. 1), collected in 1980, were analysed for ^{226}Ra, ^{210}Pb, and ^{137}Cs. The data show that the flux of atmospheric ^{210}Pb to these sediments varies between 2.2 and 10.0 mBq cm^{-2} yr^{-1}, in accord with values known for samples from non-uranium mining areas. The measured levels of ^{226}Ra in these sediments are similar to those observed earlier for locations in Lake Huron and

Figure 1. Sampling locations in Georgian Bay

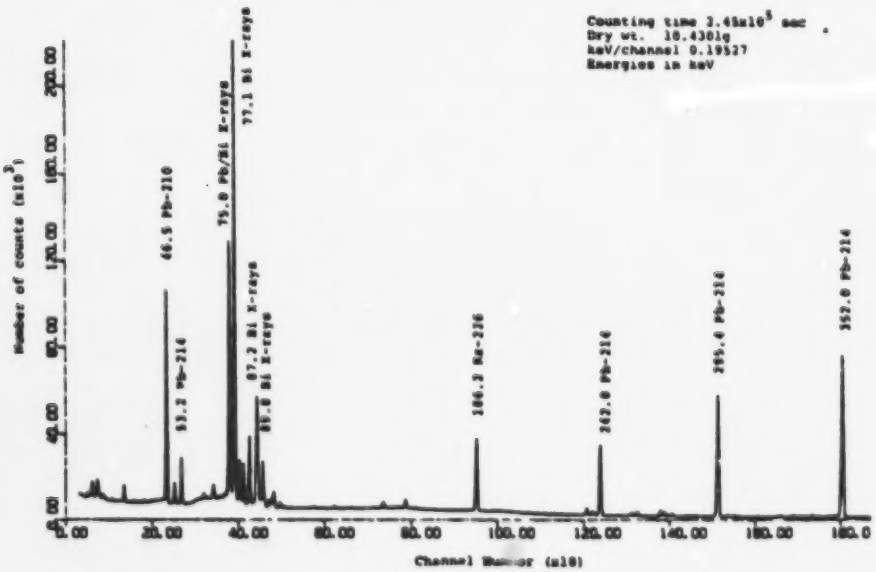

Figure 2. Low-energy gamma-ray spectrum of Langley Bay sediment

other Great Lakes. Thus, it appears that uranium mining activities in the Elliot Lake area do not have any adverse effects at these locations in Georgian Bay. In addition, these data provide first ^{210}Pb-based measurements on the sedimentation rates in Georgian Bay which are found to range between 0.13 and 0.78 mm y^{-1} (2.2 to 14.5 mg cm^{-2} yr^{-1}).

Several water and sediment samples were collected in 1983/84 from Langley Bay/Lake Athabasca. Analyses of these samples, along with those collected by EPS (W&NR) during the same field trip, are continuing for various U-series radionuclides. The newly-developed technique of low-energy gamma-ray spectrometry (Fig. 2) is amongst the analytical methods being used. Preliminary results indicate elevated levels of ^{210}Pb and ^{226}Ra in Langley Bay sediments in the vicinity of tailings pile (1557 and 1519 versus ambient levels of about 20 and 2 pCi/g, respectively).

PUBLICATIONS

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D. PRIMARILY LABORATORY STUDIES AIMED AT MEASURING PROPERTIES AND EFFECTS OF TOXIC ORGANIC CHEMICALS SO AS TO DEVELOP PREDICTIVE MODELS FOR THEIR FATE IN AQUATIC ECOSYSTEMS

CORRELATION AND PREDICTION OF CONTAMINANT HAZARDS

by

K.L.E. Kaiser, J.M. Ribo, M.E. Comba, H. Hunter,
B.M. Zaruk and G. Scott

INTRODUCTION

Ever since Rachel Carson's Silent Spring, we have generally become aware of environmental contaminants and their effects on the ecosystem. The finding of PCB's in fish by Soren Jensen in Sweden, the recognition of mirex as contaminant in fish from Lake Ontario, and the discoveries of contaminant laden leachates from dumpsites such as the Love Canal have become milestones in the search for and characterization of contaminants in our environment.

At this time, the problem no longer is so much the identification of contaminants and their sources. Rather, we are now faced with solving questions on the fates and effects of such compounds. This includes the search for mechanisms to deal effectively with the large number of chemicals already found in water, air and biota. One of such time and cost saving scientific avenues is the field of quantitative structure-activity correlations for the prediction of the environmental behavior and effects of compounds.

The necessity for such research has been recognized, Great Lakes Water Quality Agreement of 1978 (Annex 12), by the A-Base Review (Integrated Planning and Management Activity, goal 5), and has been documented by the Great Lakes Science Advisory Board (1983 Annual Report).

RESEARCH RESULTS

The effects of series of chloro-substituted benzenes and phenols and of para-substituted phenols on Photobacterium

phosphoreum have been determined with the Microtox toxicity analyzer. These effects have been correlated with published acute and sublethal toxicities of these chemicals on several species of fish, bacteria and shrimp. Moreover, the determined toxic concentrations correlate with several physico-chemical properties of the compounds, primarily the octanol/water partition coefficient (1). A representative plot of Microtox toxicity values versus the octanol/water partition coefficients of chlorophenols is shown in Figure 1.

The influence of rotational barriers of PCB's on their potential to activate the arylhydrocarbon hydroxylase enzyme system has been investigated with quantum mechanical calculations of the internal barriers. Based on the hypothesis that the active (toxic) PCB molecule must be planar, an excellent correlation was found between the experimental enzyme activation data and the fraction of planar conformers predicted from a Boltzmann like distribution (2).

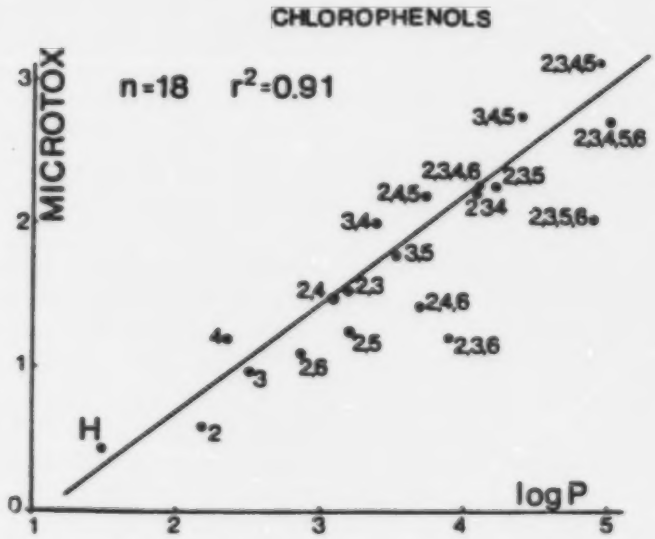

Figure 1. Plot of Microtox toxicity values versus the octanol/water partition coefficients (log P) of chlorophenols (from Ref. 1).

Several other research papers on structure-activity relationships of selected contaminants, including chlorinated phenols and benzenes (5), chlorinated anilines (6,7),

para-substituted phenols (5), and on new, rapid toxicity tests (3,4) have been presented at an international workshop on QSAR in Environmental Toxicology, chaired by K.L.E. Kaiser, at McMaster University, August 16 to 18, 1983. The proceedings of this workshop have been edited and will be published as a book on QSAR in Environmental Toxicology by the D. Reidel Publishing Company, Dordrecht, Holland, in the spring of 1984.

PUBLICATIONS

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2. Cullen, J.M. and Kaiser, K.L.E. 1984. An examination of the role of rotational barriers in the toxicology of PCB's. In QSAR in Environmental Toxicology, K.L.E. Kaiser (Ed.), D. Reidel Publ. Co., Dordrecht, Holland. (in press).

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BIODEGRADATION AND TOXICITY ASSESSMENT OF PRIORITY CONTAMINANTS

by

D. Liu, K.L.E. Kaiser, K. Thomson and K. Kwasniewska

INTRODUCTION

Recent advancement in environmental toxicology indicates that toxicity and biodegradability are important factors affecting the fate and behaviour of an organic contaminant in the environment. For instance, accumulation of a toxicant occurs only if the half-life of the toxicant is the same as or greater than the exposure interval of the biota to the chemical. Thus, such investigations are not only highly relevant to assessing hazard, an aspect important to both the Great Lakes Water Quality Agreement and the Environmental Contaminants Act, but are also essential for effective management of toxic substances in the total environment.

In this study, laboratory investigations of the bacteria-chemical interaction are coupled with research on the quantitative relationship between structure and toxicity/degradability of toxic compounds. Such information is useful in the assessment of new chemicals for their possible environmental impact.

RESEARCH RESULTS

Aniline and Marlon A were used as the model chemicals in the evaluation of various biodegradation methods. The results indicated that the test method itself could be a major factor affecting the test results.

Five oil dispersants were investigated for their persistence in aquatic environment and their rate of biodegradation determined. The results indicated that treatment of oil spills with chemical dispersants is unlikely to cause any build-up of organic contaminant in the aquatic environment.

Effects of biological activity in the mixed liquor on the operation of the activated sludge process were systematically studied. The study demonstrated that the conventional parameters (MLSS and MLVSS) used in the activated sludge process control were unreliable and a resazurin reduction procedure was thus developed for the process control with greater sensitivity, accuracy, and reliability.

The interaction between naturally-occurring humic substances and aquatic contaminants was studied using MMBT as the model "contaminant". The observed enhancement of MMBT biodegradation is probably due to the ability of fulvic acid to catalyze extracellular electron transport or function as a terminal electron acceptor.

The toxicity of chlorobenzenes to bacteria was assessed at the enzyme level and the results clearly indicated that the mechanism of chlorobenzenes biotoxicity is primarily due to their ability to uncouple the oxidative phosphorylation process.

A toxicity test, based on the use of DMSO-resazurin mixture, was developed for rapid analysis of water-insoluble chemicals for toxicity assessment up to the concentration ranges of 500 to 1000 ppm. Various chlorobenzenes and phenols were used to evaluate this method's reliability and reproducibility.

The use of whole mammalian animals in toxicology studies is currently under controversy and alternatives to investigations employing animals are actively sought.

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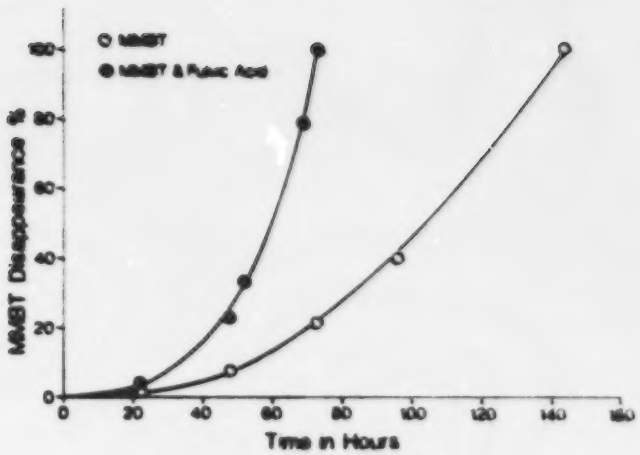

Figure 1. Enhanced MMBT biodegradation by FA in fermentor.

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CONVERSION OF MICROBIAL METABOLITES OF CHLORINATED BIPHENYLS TO INSOLUBLE PRODUCTS

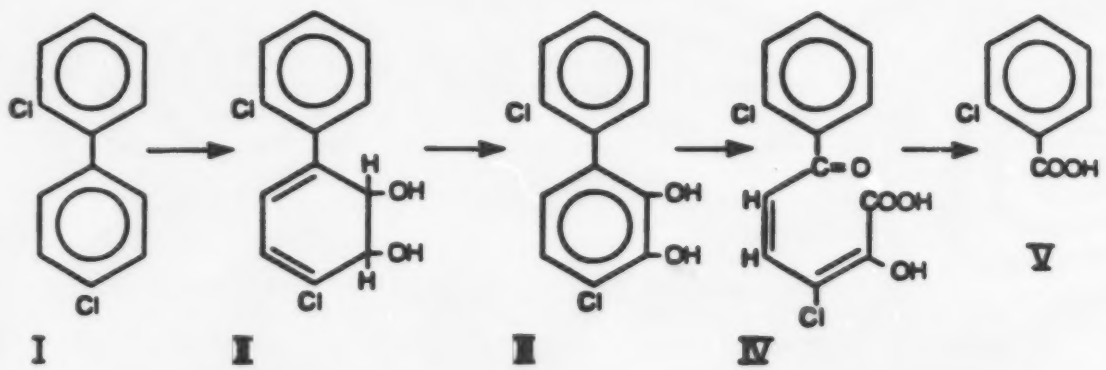
by

R.M. Baxter

INTRODUCTION

This is part of an investigation of the ways in which biochemical reactions may interact with other processes to bring about the transformation of chlorinated biphenyls in the environment.

The principal pathway for the microbial degradation of chlorinated biphenyls is shown in general outline below:



The substrate (the diagram shows 2,4-dichlorobiphenyl but several other chlorinated biphenyls behave in the same way) is converted via a dihydrodiol (II) to a diphenol (III). This undergoes

meta-cleavage of the ring to yield a bright yellow oxidation product with 2,4-dichlorobiphenyl and other 2,4-substituted biphenyls. This product is only slowly degraded to a chlorobenzoic acid (V) so the yellow compound accumulates in the medium. With certain other chlorobiphenyls the further degradation proceeds more rapidly.

In last year's report, we showed that the yellow product can undergo photochemical degradation to a chloroacetophenone which can probably be oxidized to a chlorobenzoic acid, thus bypassing the step that is limiting in the biochemical water sequence.

In the course of these investigations, it was observed that under certain circumstances cultures or suspensions of chlorobiphenyl-degrading bacteria first developed a yellow colour due presumably to a meta-cleavage product as shown above, and then the colour darkened, leading ultimately to a black insoluble material. This suggested that certain chlorobiphenyls may be irreversibly removed from the aquatic environment by conversion to insoluble materials that enter the sediment layer. This reaction has therefore been investigated further using gas chromatography then layer chromatography and UV/visible spectrophotometry.

RESEARCH RESULTS

The dark coloured product was found to be produced both by growing cultures and by resting suspensions under suitable conditions. It was not formed by cultures growing with biphenyl as a carbon source, but it was produced by cultures growing on Aroclor 1221, the only commercial chlorobiphenyl mixture capable of sustaining growth. Aroclor 1221 contains biphenyl, two monochlorobiphenyls and several dichlorobiphenyls, including 2,4-dichlorobiphenyl.

In cell suspensions, it was produced with Aroclor 1221 but not with Aroclor 1242, which yielded only the bright yellow product. Arocolor 1242 consists mostly of dichloro- and trichlorobiphenyls, including several 2,4-substituted compounds, but virtually no biphenyl and only small amounts of monochlorobiphenyls. The dark material was produced both by growing cultures and cell suspension with biphenyl and Aroclor 1242.

It appears therefore that the production of this material requires both a 2,4'-substituted biphenyl as a source of the yellow compound and an easily degraded compound such as

biphenyl or a monochlorobiphenyl which is converted to some compound which reacts with this to yield the polymeric material. It seemed possible that the compound might be a diphenol, either a dihydroxychlorobiphenyl like III or, perhaps more likely, a catechol or chlorocatechol produced by the further metabolic of benzoic acid or a monochlorobenzoic acid (V). It was found that when a solution of the yellow compound was shaken for a few hours with catechol, the solution darkened and eventually yielded a product indistinguishable from that produced for Aroclor 1221.

It was therefore concluded that the formation of the dark-coloured material probably involves the copolymerization of the yellow meta-cleavage product from a 2,4'-substituted chlorobiphenyl with a diphenol decieved from a less highly chlorinated compound.

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BIOAVAILABILITY OF ORGANIC CONTAMINANTS IN SEDIMENTS

by

B.G. Oliver and K.D. Nicol

INTRODUCTION

One of the important sinks for organic contaminants discharged into the Great Lakes are bottom lake sediments. Eventually continued sedimentation will bury contaminant bearing sediments, but this process is slow since sedimentation rates in the lakes are low (between 0.1 and 10 mm/year). Oligochaete worms, which live in the bottom sediments, have been shown to recycle sediments down to a depth of 80 to 100 mm. Therefore, it will require between 10 and 1000 years, depending on location, for contaminated sediments to be buried below this bioturbation zone. Before burial, contaminants on sediments may be available for biological uptake directly by biota such as oligochaetes or may be made available by resuspension of the sediments into the water column where the contaminants may be desorbed. The object of this project is to find out what portion of the organic contaminants in sediments is bioavailable by these two pathways.

RESEARCH RESULTS

The biouptake by oligochaete worms of several chlorinated compounds from "naturally" contaminated Lake Ontario sediments has been studied in laboratory aquariums (1). The concentration factor, CF (worm concentration/sediment concentration) varied considerably with chemical structure and sediment type. For example, CF's varied from 0.06 for 1,2,4,5-tetrachlorobenzene to 6.7 for octachlorostyrene - a difference of over 2 orders of magnitude. Because of the different CF's for the various chemicals the oligochaete worms contained a different chemical mixture than the sediment in which they lived. For example, the worms contained more octachlorostyrene and less

chlorobenzenes than the sediments, and the PCB isomer composition of the worms was different from isomer composition of the sediments. Thus, worm predators such as small fish will be subjected to a different chemical mixture than is found in the sediments. Macroinvertebrate analysis appears essential for fish chemical exposure models.

The desorption of chlorobenzenes and PCBs from experimentally and "naturally" contaminated sediments has been studied. Desorption rates were much faster at higher temperature, but significant desorption does occur even at low temperatures. Chemical structure has been shown to have a strong influence on desorption rates.

PUBLICATIONS

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TOXICITY AND BIODEGRADABILITY OF ORGANIC ENVIRONMENTAL CONTAMINANTS

by

K. Kwasniewska, K.L.E. Kaiser and D. Liu

INTRODUCTION

Study on the toxicity and biodegradability of organic compounds is an essential aspect for the assessment of toxic substances in the environment. Due to the complexity involved in the interaction between biota and toxicants, it is also necessary to investigate the fate and behaviour of chemicals in the total ecosystem including bioaccumulation in the food chain of environmental biota.

Determination of toxicity and biodegradability of existing and new chemicals are highly relevant to the hazard assessment, an aspect of the Environmental Contaminants Act.

Yeast and fungi, in particular, are directly involved in the removal and bioconcentration of toxic substances from the environment. For that reason, current research efforts are directed towards the examination of the effects of contaminants on important aquatic species, such as yeast or yeast like fungi. They are similar to higher eukaryotes (such as mammals) in both cellular structure and metabolic behaviour. As a result, they offer certain biochemical, metabolic and genetic advantages over bacteria. Furthermore, yeasts or yeast-like fungi are ubiquitous organisms and have been shown to possess mechanisms to cope with various physical and chemical stresses. Such characteristics make yeasts useful and important organisms for the study of contaminant toxicity and degradation.

RESEARCH RESULTS

This study has resulted in three papers.

Ten chemicals including five chlorophenols and five parasubstituted phenols, have been tested for their toxicity to fermentative and oxidative yeast strains. The reults indicate that oxidative strains were the more sensitive ones and a quantitative structure-toxicity relationship was found (Publication No. 1).

The growth inhibition of 8 chloro-anilines on four strains of yeast has been investigated. The results demonstrate the applicability of using yeasts as microorganisms to study structure-activity correlations between the toxicities of such chemicals to yeasts and various physico-chemical parameters (Publication No. 2).

The biodegradation of crystal violet (hexamethyl-p-rosaniline chloride) on aniline dye, was studied using both, oxidative and fermanetative yeasts. The results indicate that two oxidative yeast species (Rhodotorulae), reported previously (Kwasniewska and Kaiser 1983) were more sensitive to a number of selected chemicals that the fermentative species S. cerevisiae. However, the present biodegradation study shows that only oxidative strains of yeast were capable of degrading the dye crystal violet. Since crystal violet dye is known to be persistent in the environment and is a mutagen. The biodegradability of this dye by the oxidative yeast clearly demonstrates that yeast or yeast like fungi play a significant role in the removal of contaminants from the aquatic environment (Publ. No. 3).

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E. PROJECTS AIMED AT MODELLING THE RATE OF ACIDIFICATION OF RIVER BASINS AND RESOLVING THE GEOCHEMICAL PROCESSES CONTROLLING THIS RATE AND ITS EFFECTS

HYDROGEOCHEMICAL RESPONSES OF THE TURKEY LAKES WATERSHED TO ACID PRECIPITATION

by

D.S. Jeffries, R.G. Semkin, R. Neureuther,
J. Longlade and M.D. Jones

INTRODUCTION

The Turkey Lakes Watershed (TLW) has been established as one of five calibrated watersheds in eastern Canada with the purpose of determining the effects of acidic deposition on sensitive terrain. Specifically, information from this study will be used to quantify pollutant pathways and to define cause-effect relationships from which predictive models of ecosystem effect can be developed and verified. The TLW is a hydrologically gauged, headwater basin located 50 km north of Sault Ste. Marie, Ontario. It is 10.5 km^2 in area and contains several individually gauged sub-basins. This basin is unique among the 5 calibrated watersheds for its combination of moderate pollutant deposition, moderate terrain sensitivity, mixed hardwood forest type, and "chain of lakes" approach. Information obtained by this study and all others associated with the TLW is summarized in the Turkey Lake Watershed Unpublished Report Series (1).

RESEARCH RESULTS

Acquisition, storage and manipulation of the data required for calculation of lake mass balances has continued. Daily flow data for the six lake (or watershed) outflow stations and 14 headwater feeder streams have been obtained for 1982 to compliment the existing 1980/81 data set. Similarly, collection of the corresponding data for stream chemistry has also continued. All of the above data have been coded and stored in the computerized national water quality data base (NAQUADAT) at CCIW.

A specialized set of computer programs have been developed which combine the daily flow values with the intermittent chemistry data to provide an estimate of stream loadings which will be used to calculate mass budgets in the next year.

For example, monthly total stream discharge and calculated alkalinity loadings for 1982 at station S1 and Turkey Lake outlet (e.g., S4) are given in Table 1. The corresponding daily values are presented in Figure 1 to illustrate the variability observed for each parameter. Unusual hydrological conditions were observed in 1982; these are manifested in Figure 1 by a very late and low intensity peak in spring runoff, and very high short-duration peaks in flow caused by an exceedingly wet autumn. The lower (e.g., Turkey Lake outlet) station naturally exhibits the more "damped" response to these conditions. The alkalinity load clearly shows the effect of spring acidification and/or runoff dilution. Relative to flow, the alkalinity load is depressed during the spring when soil-water interaction is minimal, while in the autumn, when there is less restriction on this interaction, alkalinity load simply follows flow (e.g., alkalinity concentrations remain reasonably constant).

TABLE 1. MONTHLY STREAM DISCHARGE AND ALKALINITY LOAD IN 1982 FOR STATIONS S1 AND THE TURKEY LAKE OUTLET (E.G., S4) IN THE TURKEY LAKES WATERSHED. THE BASIN AREA ABOVE S4 IS APPROXIMATELY 4-FOLD GREATER THAN THAT ABOVE S1.

	Discharge ($m^3 \times 10^3$)		Alkalinity Load (meq $\times 10^3$)	
1982	S1	S4	S1	S4
January	33.8	222	2.4	43.9
February	21.7	145	1.4	30.5
March	44.2	174	3.0	34.4
April	546	1400	10.8	198
May	585	2010	12.7	266
June	21.7	122	1.4	23.5
July	11.7	83.4	0.8	17.4
August	2.6	41.9	0.2	11.0
September	156	369	7.4	73.3
October	391	1440	12.9	271
November	278	1100	7.4	202
December	165	713	4.6	118

Data for lake composition have also been entered into NAQUADAT, edited and a summary report produced (2) for major ions covering the period January 1980 to May 1982. The lakes are all oligotrophic to mesotrophic in character. The three lakes having maximum depth between 10 and 15 m (e.g., Batchawana N and S, and L. Turkey) all devlop anoxic hypolimnia during the summer. All of the above data are currently being used to develop predictive models for basin response to LRTAP.

Finally, physical data collected in the watershed (e.g., meteorology, lake temperature, etc.) have been summarized through June 1983. Lake evaporation calculated from this data using an energy budget approach for 1982 was extremely low ranging from 36.6 cm yr^{-1} for Little Turkey Lake to 43.6 cm yr^{-1} for Batchawana Lake North. Comparison with estimates from measured water budgets will be used to verify these results.

PUBLICATIONS

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GEOCHEMICAL CONTROLS OF AQUATIC SYSTEM RESPONSE TO DEPOSITION OF ATMOSPHERIC POLLUTANTS

by

D.S. Jeffries, R.G. Semkin and B.G. Oliver

INTRODUCTION

The departmental objective to "determine the ability and capacity of the ecosystem of Canada to withstand contamination due to the long-range transport of air pollutants" is being addressed through study of a specific watershed in northern Ontario, e.g., the Turkey Lakes Watershed (TLW). The purpose is to determine the factors controlling the degree and rate of acidification of drainage basins and associated lakes by measuring the geochemical response of the TLW to the impact of acids.

RESEARCH RESULTS

The study has focussed on 2 activities. First, determination of the importance of short-term events of acidification by intensively monitoring the major ion chemistry of the snowpack, lakes and streams prior to and during spring snowmelt, and second, establishing a study of Al mobilization and speciation in a headwater sub-basin of the TLW.

The investigation of factors controlling changes in stream and lake composition during snowmelt may be divided into three subprojects.

First, accumulation and decline of the snowpack in the Turkey Lakes Watershed was investigated at several locations by core sampling on a weekly basis. Analysis of water equivalent and major ion composition of the cores permits evaluation of the temporal and spatial variability present in the watershed. When combined with meteorological and deposition data also collected in the watershed (as part of mass balance studies), the factors

influencing contaminant release was delineated. For example, Figure 1 shows the accumulation in and loss of water from the snowpack for H^+, SO_4^{2-}, NO_3^-, and NH_4^+ during 1982. The contaminants stored in the snow pack (particularly H+) were rapidly and preferentially removed (with respect to water) at the beginning of the melt period. The snowpack content of SO_4^{2-}, NO_3^-, and NH_4^+ exhibited large, short-term variability in response to specific rainfall events.

Second, the hydrologic and chemical responses of lakes and streams to the snowmelt were studied by intensive monitoring throughout this critical period. Automatic samplers and helicopters are required to complete this sampling, particularly during the late-melt period. Particular attention was paid to the variation occurring in pH and the concentrations of alkalinity, SO_4^{2-}, NO_3^- and other cations. Use of the Turkey Lakes Watershed permits evaluation of the snowmelt effect across a range of terrain sensitivity (e.g., most sensitive at the top and least sensitive at the bottom). The variation in stream composition at station S1 which occurred in 1981 is shown in Figure 2. Spring runoff produced a substantial decline in major cation and alkalinity concentrations, a relatively smaller decrease in SO_4^{2-}, a small increase in NO_3^- and a large (5-fold) increase in H^+. Peak stream acidity occurred after peak stream flow which differs from observations made in Norway but are similar to those make in Muskoka-Haliburtor, Ontario. Results from both of the above sub-projects have been reported (1).

Third, the influence of within snowpack movement of water and major ions on the eventual release to soils and streams is being studied through use of a snow corral - in essence a plastic covered slope in which water percolating down to the soil interface is channelled off to the side at various points down the slope. The proportion of water and ions emerging at different levels will give information on the degree of soil-meltwater interaction which can occur prior to discharge to the streams. Actual changes in meltwater composition as the meltwater passes through the soils is monitored using trough and porous cup lysimeters. For all of the snowmelt studies, ion analyses are performed using standard procedures (DOE Methods Manual) at Sault Ste. Marie, except for snow samples which are determined by ion chromatography at NWRI. During the past year the snow corral has been constructed on a north-facing slope in the Little Turkey Lake sub-basin and meltwater sampling will commence with the 1984 snowmelt.

Finally, a plan has been established for study of the spatial and temporal variations in Al concentration and speciation

in the Batchawana Lake South sub-basin. Sampling will be coupled with the existing sampling program for snowmelt (described above) and the regular mass balance studies. All samples will be collected in plastic containers and analyzed for acid soluble Al, labile monomeric Al, and organically-bound Al using the oxine-MIBK forms of Al will be separated by dialysis (also in the field). An extensive review of existing Al speciation methodology was performed prior to selecting the oxine-MIBK procedure for use in the TLW. Field sampling was initiated in February 1984.

In addition to the above, a previous study was completed with publication of a paper on the contribution of humic acids to the acidity of coloured, natural waters (2). Briefly, the carboxylic acid content of specific organic rich waters was investigated in detail through extraction, concentration, and titration. Once complete, a relationship was recognized in which the carboxyl content of waters could be related to the organic carbon content and this relationship was checked (and verified) for waters from diverse locations throughout North America. The dissociation behavior of carboxyl groups on humic acids was found to be a function of pH. Combining the information on carboxyl content and dissociation behavior, it is possible to predict the quantity of organic anions present and thereby predict the supply of H^+ arising from the organic material present in the waters.

PUBLICATIONS

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POOR

QUALITY

ORIGINAL